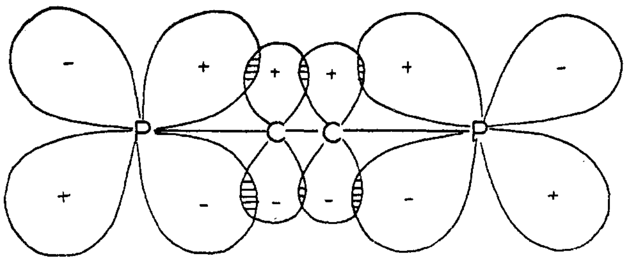

Figure 1.—pπ–dπ (C–P) overlap in the linear skeleton of DPPA.

phine (1.83 Å) and trimethylphosphine (1.85 Å).[24] It should be remembered, however, that while this result may suggest P(dπ)–C(pπ) interaction, a shortening of the P—C bond would be expected since the covalent radius of an sp-hydridized carbon atom is 0.07 Å smaller than that of an sp^3 atom.

If only σ-bonding P→M was important in these copper complexes, a small but noticeable shift to lower frequency of ν(C≡C) would be expected on complexation since σ donation of P→M would effectively increase the electronegativity of the phosphorus atom. Conversely strong dπ–dπ interaction between filled copper dπ orbitals and empty phosphorus dπ orbitals would tend to weaken the interaction pπ–dπ (C–P) and result in a stronger C≡C bond and a consequent high-frequency shift for ν(C≡C).

Extensive M(dπ)–P(dπ) bonding is to be expected with III since preliminary work suggests that this ligand is at least as effective as phosphites in replacing carbon monoxide from metal carbonyls.[45] The Raman results in Table IV confirm this hypothesis. Compounds of the type $(AuX)_2DPPA$ show the largest ν(C≡C) shifts in agreement with the fact that only one phosphorus atom per gold atom is available for back-bonding compared with three or four in the remaining complexes. Also, the linear geometry of these species facilitates Au(dπ)→P(dπ) back-bonding. Values for $(AuI)_2(DPPA)_3$ and $(AuNCS)_2(DPPA)_3$ are very close to the range 2120–2125 cm^{-1} for copper(I) complexes of the same type suggesting that Au(I) and Cu(I) have similar π-bonding abilities with phosphorus. As expected the compounds $(AuBF_4)_2(DPPA)_4$ and $(AuPF_6)_2(DPPA)_4$ have the lowest ν(C≡C) frequencies consistent with the presence of four phosphorus π acceptors per gold atom.

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The Interaction of Mercury(II) Salts with Pyridine 1-Oxide

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The interaction of pyridine 1-oxide with mercury(II) salts yields coordination compounds of three different types: $[Hg(C_5H_5NO)_6]A_2$, $[Hg(C_5H_5NO)_2A_2]$, and $[Hg(C_5H_5NO)A_2]_2$. Infrared spectral data, conductivities, and molecular weights indicate that compounds of the type $[Hg(C_5H_5NO)A_2]_2$ are dimeric with pyridine 1-oxide bridging. Compounds of the types $Hg(C_5H_5NO)_6A_2$ and $Hg(C_5H_5NO)_2A_2$ are octahedral. $Hg(C_5H_5NO)_2(CN)_2$ does not appear to fit the above pattern. The type of compound obtained when mercury(II) salts interact with pyridine 1-oxide is determined by the nature of the anion.

Introduction

During recent years pyridine 1-oxide has been found to be a versatile Lewis base, which coordinates through the oxygen atom.[1-6] It has been suggested that pyridine 1-oxide also acts as an excellent π-electron acceptor *via* back-donation,[7,8] although attempts to correlate the strength of the interaction with the π-electron acceptor ability for substituted pyridine 1-oxides were only partially successful. The occurrence of back-donation in these compounds was disputed in recent communications.[9] Also of interest with the coordination compounds of pyridine 1-oxide are its ability to act as a bridging group, exemplified by $[CuA_2(C_5H_5NO)]_2$,[10] and its ability to give complexes

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TABLE I

COORDINATION COMPOUNDS OF PYRIDINE 1-OXIDE AND MERCURY(II)

Anion	pyO/Hg ratio	Mode of prepn	Mp, °C	% mercury		$\nu(NO)_1$, cm^{-1}	$\nu(NO)_2$, cm^{-1}	Equiv cond (4×10^{-4} M)
				Calcd	Found			
BF_4	6	B	156–157	21.23	21.24	1211	830	177
ClO_4[a]	6	A, B	168–169	20.67	20.65	1213	832	178
PF_6	6	B	173–174	18.85	18.55	1210	830	161
AsF_6	6	B	173–174	17.40	17.16	1212	832	145
SbF_6	6	B	169–170	16.14	16.85	1210	830	198
Cl[b,c]	1	A	167–168	54.72	54.64	1206	830	50
Br[c]	1	A	162–163	44.04	44.08	1200	826	41
I[c]	1	C	141–142	36.50	36.60	1198	825	34
SCN	1	C	131	48.74	49.57	1203	829	. . .
NO_3[a]	2	B	134–135	38.91	39.64	1204	829	34
CF_3CO_2	2	B	116–117	32.40	32.29	1203	808	16
CCl_3CO_2	2	B	100–101	28.01	27.34	1200	807	11
CN	2	A	125–126	45.30	45.56	1217	833	0.25

[a] $Hg(C_5H_5NO)_6(ClO_4)_2$ and $Hg(C_5H_5NO)_2(NO_3)_2$ were previously prepared by Carlin, *et al.*[1,14] [b] $Hg(C_5H_5NO)Cl_2$ was reported earlier but was not characterized.[11] [c] Halides, determined gravimetrically as the silver salts: calcd for $Hg(C_5H_5NO)Cl_2$, 19.34%; found, 19.12%; calcd for $Hg(C_5H_5NO)Br_2$, 35.08%; found, 37.47%; calcd for $Hg(C_5H_5NO)I_2$, 46.44%; found, 46.19%.

where the central atom exhibits its maximum coordination number. Carlin has suggested that the tendency to yield compounds with the maximum coordination number, which has been noted for several systems,[1,2,5] is the result of the small steric requirement of pyridine 1-oxide. These facts, together with the isolation of $[Hg(C_5H_5NO)_6](ClO_4)_2$,[1] $(CF_3)_2Hg(C_5H_5NO)_2$,[4] and $HgCl_2(C_5H_5NO)$,[11] led us to believe that pyridine 1-oxide would be an excellent ligand for use in the investigation of factors which affect the structure and bonding in coordination compounds of mercury(II). Consequently the investigation of the interaction of pyridine 1-oxide with mercury(II) was begun. In this paper the preparation and characterization of the coordination compounds formed when pyridine 1-oxide interacts with various mercury(II) salts are reported.

Experimental Section

Chemicals.—Except for those described below, all chemicals were reagent grade or Eastman White Label and were used without further purification. Pyridine 1-oxide (Eastman practical grade) was purified and dried by repeated sublimation *in vacuo* at 40°. The purified pyridine 1-oxide was handled within a drybag for experiments where the presence of water could be detrimental. The acetonitrile used for conductivity studies was purified by shaking with magnesium sulfate followed by fractional distillation from calcium sulfate. The fraction distilling between 79.9 and 80.1° was retained. The benzene used as solvent in the molecular weight studies was thiophene-free benzene which was dried by distillation from a sodium-lead alloy just prior to use.

Preparation of Compounds.—In the first method (method A), a solution of the mercury(II) salt was dissolved in alcohol and an excess of pyridine 1-oxide as an alcoholic solution was added with stirring. Either methanol or 95% ethanol was used as solvent with no apparent difference other than differences in solubility. When necessary, a small amount of the corresponding acid was used to prevent hydrolysis. The precipitates, which usually formed immediately, were filtered and washed with two or three small portions of alcohol. The precipitates were dried in an oven at 100° for 3–5 hr or in a desiccator over activated alumina for 2–3 days. The coordination compounds of the mercury(II) halides were further purified by sublimation *in vacuo* at 40°. In some cases, particularly $[Hg(C_5H_5NO)_6](ClO_4)_2$ and $[Hg(C_5H_5NO)_6](BF_4)_2$, the compounds were purified by recrystallization from 95% ethanol. When a particular mercury(II) salt was not available, it was prepared *in situ* (method B) by adding the least possible amount of a concentrated aqueous solution of the corresponding acid to an alcoholic slurry of mercury(II) oxide (or by adding an alkali metal salt of the anion to an alcoholic solution of mercury(II) acetate or nitrate). An alcoholic solution of pyridine 1-oxide was then added to this mixture. The precipitates were filtered, washed, and dried as described for method A. When a particular mercury(II) salt was very insoluble, it was added to a concentrated solution of pyridine 1-oxide in alcohol (method C) and the mixture was heated until the salt dissolved. The coordination compound, which precipitated upon cooling, was treated as described for method A.

The coordination compounds prepared in this investigation and the corresponding analytical data are listed in Table I. Mercury was determined spectrophotometrically, as HgI_4^{2-},[12] or gravimetrically, as $[Cu(en)_2]HgI_4$.[13]

Infrared Spectra.—Infrared spectra were obtained as Nujol mulls on polyethylene film or sodium chloride plates, using a Perkin-Elmer 621 spectrophotometer. Polystyrene film was used as an external standard.

Conductivity.—An Industrial Instruments conductivity bridge (repeatability 0.1%) was used to determine the conductivity in acetonitrile of the compounds prepared in this investigation. Plots of equivalent conductivity *vs.* the square root of concentration over the 5×10^{-6} to 8×10^{-4} M range fell into two distinct categories as illustrated in Figure 1. Since extrapolations to infinite dilution would be meaningless for most of these plots, the conductivities at 4×10^{-4} M are included in Table I.

Molecular Weights.—Using a freezing point depression method, the molecular weights of $HgCl_2(C_5H_5NO)$, $HgBr_2(C_5H_5NO)$, and $HgI_2(C_5H_5NO)$ in benzene solution were found to be 520, 800, and 1160, respectively. A thermistor bridge calibrated with recrystallized naphthalene was used to determine the freezing points. The low solubility of the coordination compounds in benzene limited the sensitivity of the method to 10%.

Results and Discussion

The interaction of pyridine 1-oxide with a variety of mercury(II) salts yields compounds containing coordinated pyridine 1-oxide. In general, these compounds precipitated immediately upon mixing the

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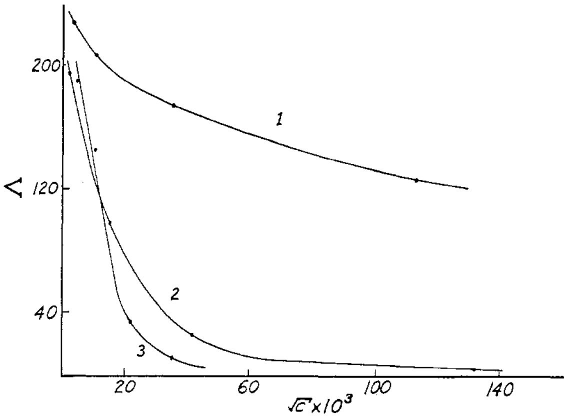

Figure 1.—Equivalent conductivity of: $[Hg(pyO)_6](BF_4)_2$ (curve 1) which is typical of compounds of the type $Hg(pyO)_6A_2$; $[Hg(pyO)Br_2]_2$ (curve 2) which is typical of compounds of the type $[Hg(pyO)A_2]_2$; and $Hg(pyO)_2(CF_3CO_2)_2$ (curve 3) which is typical of compounds of the type $Hg(pyO)_2A_2$.

reagents; however, it was occasionally necessary to refrigerate the solution, evaporate a portion of the solvent, or add acetone or diethyl ether before the product would precipitate. Numerous attempts were made to prepare coordination compounds of pyridine 1-oxide and either mercury(II) fluoride or mercury(II) acetate. No evidence of the formation of a coordination compound containing either anion was obtained. The only products which could be isolated during these attempts were the reactants or hydrolysis products.[1,14]

The coordination compounds which were obtained in this study exhibit three different stoichiometries, HgA_2L_6, HgA_2L_2, and HgA_2L. Since the structure and properties of these compounds correlate well with the stoichiometry, each stoichiometry will be discussed separately.

Compounds of the Type $Hg(C_5H_5NO)_6A_2$.—Coordination compounds of the type $Hg(C_5H_5NO)_6A_2$ (Table I) are characterized by anions which have essentially no electron-donor ability toward mercury(II) and by relatively small changes in the properties of the compounds on changing from one compound to another. The infrared spectrum of the coordinated pyridine 1-oxide (Table I) is the same within experimental error for all five of the compounds.[15] The infrared spectra of the anions indicate that the anions do not interact with the mercury in the solid state. X-Ray powder patterns[16] for these compounds were indexed in terms of a tetragonal unit cell. Both the magnitude of the conductivity in acetonitrile and the variation of the conductivity with concentration for these compounds are in the range expected for 2:1 electrolytes.[17] This indicates that the correct description of these compounds in solution as well as in the solid state is in terms of the ions $Hg(C_5H_5NO)_6^{2+}$ and ClO_4^-.

An extension of the usual radius ratio rules for ionic compounds[18] would predict a rutile-like lattice for ionic compounds of the type MA_2 when the cation to anion radius ratio becomes large. Exceedingly large cation to anion radius ratios would lead to instability of the tetragonal lattice. The failure of $[Hg(C_5H_5NO)_6]F_2$ to form could indicate that the fluoride ion is too small to stabilize the lattice. Indeed, the larger unit cell and lower melting point for $[Hg(C_5H_5NO)_6](BF_4)_2$ ($a = b =$ 19.7 Å, $c =$ 8.7 Å, and mp 157°) compared to those of $[Hg(C_5H_5NO)_6](ClO_4)_2$ ($a = b =$ 19.1 Å, $c =$ 7.9 Å, and mp 169°), which indicates a decrease in the stability of the lattice, suggest that BF_4^- is approaching the limiting size for a stable lattice.

Compounds of the Type $[Hg(C_5H_5NO)A_2]_2$.—Compounds of the type $[Hg(C_5H_5NO)A_2]_2$ (Table I) are characterized by anions (Cl, Br, I, or SCN) that are relatively strong electron-pair donors toward mercury. The low conductivity of these compounds in acetonitrile (Table I) as well as the variation of this conductivity with concentration (Figure 1, curve 2) indicates that the anions are strongly bonded to the mercury atom. The infrared spectra of the coordinated pyridine 1-oxide in these compounds (Table I)[15] depend on the anion further indicating that the anion is a part of the primary coordination sphere.

The molecular weights obtained for these compounds (*vide supra*) indicate that they are dimeric in benzene solution. Dimers of this stoichiometry have been reported[19] previously for coordination compounds of mercury in which either the anion or the neutral ligand molecule acts as the bridging ligand. Compounds of the type $Cl_2ML_2MCl_2$, where M is a metal ion and L is a neutral ligand, exhibit two metal–chlorine stretching bands in the 300–345-cm^{-1} region.[20] For example $Cl_2Cu(pyO)_2CuCl_2$ has copper–chlorine stretching bands at 330 and 311 cm^{-1}.[10] Compounds of the type $LClMCl_2MClL$ exhibit one metal–chlorine stretching band in the 280–320-cm^{-1} region[20] (presumably the remaining metal–chlorine bands are below 200 cm^{-1}). For example, $(C_6H_5)_3AsClHgCl_2HgClAs(C_6H_5)_3$ has a single band at 288 cm^{-1}.[10] $[HgCl_2(C_5H_5NO)]_2$ exhibits mercury–chlorine stretching bands at 335 and 310 cm^{-1}, indicating that pyridine 1-oxide is the

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(14) R. Carlin and M. J. Baker, *J. Chem. Soc.*, 5008 (1964).

(15) Only those absorption bands which have been reported to involve the NO bond[6] are reported here. Originally the band at 1268 cm^{-1} was assigned to the NO stretching mode and the 841-cm^{-1} band was assigned to an NO bending mode; however, a recent normal-coordinate analysis (G. Costa and V. Galasso, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **37**, 289 (1964)) has shown that both of these bands involve NO stretching.

(16) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965); Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760 (1965).

(17) X-Ray powder patterns were obtained on a Philips Norelco diffractometer using copper Kα radiation. The samples were mixed with 2 parts of dried starch, encased in 0.3-mm glass capillaries and irradiated for 7–9 hr in a Philips Norelco Type 52058 camera. Line spacings were determined to within ±0.005 cm with the aid of an illuminated film reader. The indexing procedure, which accounted for all of the observed lines, indicated a tetragonal lattice for all five compounds. The cell dimensions are (Å): $Hg(C_5H_5NO)_6(BF_4)_2$, a = 19.7, c = 8.7; $Hg(C_5H_5NO)_6(ClO_4)_2$, a = 19.1, c = 7.8; $Hg(C_5H_5NO)_6(PF_6)_2$, a = 19.6, c = 8.4; $Hg(C_5H_5NO)_6(AsF_6)_2$, a = 19.5, c = 8.9; $Hg(C_5H_5NO)_6(SbF_6)_2$, a = 19.7, c = 9.1.

(18) The usual model used in discussing radius ratio rules is a lattice of large anions in mutual contact with the cations in the interstitial holes. For very large cations ($(r_+/r_-) > 1$) the model should be reversed giving a lattice of cations in mutual contact with the anions in the interstitial holes.

(19) D. Grdenic, *Quart. Rev.* (London), 303 (1965).

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bridging ligand and the formula is $Cl_2Hg(C_5H_5NO)_2HgCl_2$. $[Hg(SCN)_2pyO]_2$ exhibits three ν(CN) bands at 2120, 2130, and 2138 cm^{-1}. These bands occur at the upper limit of the region where ν(CN) of S-bonded terminal SCN groups occur but appreciably below the range for bridging SCN groups (2150–2182 cm^{-1})[21] indicating that pyridine 1-oxide is the bridging ligand. The existence of three bands probably indicates some distortion in the molecule. ν(HgBr) and ν(HgI) occur at frequencies below the range of our instrument; however, the bromide and iodide compounds would be expected to have the same structure as the chloride.

Compounds of the Type $Hg(C_5H_5NO)_2A_2$.—Three of the five compounds which have been prepared with the stoichiometry $Hg(C_5H_5NO)_2A_2$, $Hg(C_5H_5NO)(NO_3)_2$, $Hg(C_5H_5NO)_2(CF_3CO_2)_2$, and $Hg(C_5H_5NO)_2(CCl_3CO_2)_2$, have oxyanions which are weak electron-pair donors. Since the anions in each of these three compounds can act as bidentate ligands, it would be tempting to propose that these compounds consist of monomeric molecules in which the mercury atom is octahedrally surrounded by six oxygen atoms, two from the pyridine 1-oxide molecules and four from the anions. Indeed, the conductivity of these compounds (Table I) and the infrared stretching modes of the anions indicate that the anions are strongly coordinated to the mercury atom. Nakamoto, *et al.*,[22] suggested that unidentate bonding to an acetate moiety would yield structurally different oxygen atoms with a greater difference in the two carbon–oxygen stretching modes than would be expected for the structurally identical oxygen atoms of the bidentate bonded moiety or the free anion. The separation in the two ν(CO) modes for $Hg(C_5H_5NO)_2(CF_3CO_2)_2$, 265 cm^{-1}, and $Hg(C_5H_5NO)_2(CCl_3CO_2)_2$, 339 cm^{-1}, is decidedly smaller than the separation in the trifluoroacetic acid (595 cm^{-1})[23] and is comparable to the separation found in the free trifluoroacetate ion (240 cm^{-1} for KCF_3CO_2).[23] Therefore, the two acetate moieties are acting as bidentate ligands in the compounds $Hg(CF_3CO_2)_2(C_5H_5NO)_2$ and $Hg(CCl_3CO_2)_2(C_5H_5NO)_2$. Infrared spectra will not distinguish between unidentate and bidentate bonding of the nitrate ion; however, the available data are consistent with bidentate bonding of the anion in $Hg(C_5H_5NO)_2(NO_3)_2$.

The other two compounds containing 2 mol of pyridine 1-oxide/mol of mercury, $(CF_3)_2Hg(C_5H_5NO)_2$ and $Hg(C_5H_5NO)_2(CN)_2$, cannot fit a model involving bidentate bonding of the anion. These two compounds could involve tetrahedral coordination of the mercury atom, which was originally suggested for $(CF_3)_2Hg(C_5H_5NO)_2$,[4] or octahedral coordination through pyridine 1-oxide bridging. The single NO stretching band observed for these compounds, as well as the low molecular weight (264) of $Hg(C_5H_5NO)_2(CN)_2$ in nitrobenzene, seems to disfavor bridging in these two compounds.

The interaction of pyridine 1-oxide with mercury(II) salts yields coordination compounds which can be divided into three classes with each class having a characteristic stoichiometry and set of properties. Unlike the previously described series[2,3] of coordination compounds of copper(II) and pyridine 1-oxide, no mercury(II) salt formed more than one coordination compound with pyridine 1-oxide. During the course of this investigation, numerous unsuccessful attempts were made to prepare $Hg(C_5H_5NO)_2(ClO_4)_2$, $Hg(C_5H_5NO)_6(NO_3)_2$, and $Hg(C_5H_5NO)_2Cl_2$; however, no indication of the existence of these compounds was obtained. In the copper(II) system variation of the reaction conditions readily yielded different coordination compounds which is the behavior expected for a system where two ligands are competing for positions in the coordination sphere. The stoichiometry and thus structure of the coordination compounds of mercury(II) appear to be determined solely by the nature of the anion. This could indicate a change in the pyridine 1-oxide to mercury(II) bond on going from noncoordinating anions to coordinating anions. The nature of the mercury–oxygen bond in these compounds is being investigated more fully.

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[21] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 173–176.

[22] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayshi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

[23] N. B. Colthup, L. H. Daly, and S. E. Wiberky, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 381.